Energy, Mines and Resources Canada
Énergie, Mines et Ressources Canada

CANMET
Canada Centre for Mineral and Energy Technology
Centre canadien de la technologie des minéraux et de l'énergie

+525^{o}C PITCH CONTENT VERSUS MICROCARBON RESIDUE:

A CORRELATION FOR CHARACTERIZING REACTION PRODUCTS OBTAINED BY HYDROCRACKING BITUMENS, HEAVY OILS, AND PETROLEUM RESIDUA

M. Ternan and J.F. Kriz
Synthetic Fuels Research Laboratory

SEPTEMBER 1989

ENERGY RESEARCH LABORATORY
DIVISION REPORT 89-53(J)

This work was supported in part by the federal panel on Energy Research and Development (PERD)

+525°C PITCH CONTENT VERSUS MICROCARBON RESIDUE:

A CORRELATION FOR CHARACTERIZING REACTION PRODUCTS OBTAINED BY HYDROCRACKING BITUMENS, HEAVY OILS, AND PETROLEUM RESIDUA

by

M. Ternan* and J.F. Kriz

Energy Research Laboratories / CANMET
Energy, Mines and Resources Canada
Ottawa, Ontario, K1A 0G1

Key Words: microcarbon residue, pitch, distillation, hydrocracking, heavy oil, bitumen

It is proposed that this manuscript be considered for publication in the "Petroleum Chemist's Notebook" section of the AOSTRA Journal of Research.

+525°C PITCH CONTENT VERSUS MICROCARBON RESIDUE:

A CORRELATION FOR CHARACTERIZING REACTION PRODUCTS OBTAINED BY HYDROCRACKING BITUMENS, HEAVY OILS, AND PETROLEUM RESIDUA

by

M. Ternan* and J.F. Kriz

Energy Research Laboratories / CANMET
Energy, Mines and Resources Canada
Ottawa, Ontario, K1A 0G1

ABSTRACT

An empirical correlation between the wt % microcarbon residue and the wt % +525°C pitch in liquid products from hydroprocessing is reported. Prediction of the +525°C pitch content from experimental measurements of microcarbon residue will make characterization of hydroprocessed liquids simpler and faster. The data in the correlation were obtained from thermally and catalytically hydrocracked heavy oil and bitumen samples. In addition, one result with a coprocessed liquid product was included.

INTRODUCTION

The primary objective of all processes for upgrading bitumens, coals, heavy oils, and petroleum residua is to decrease the molecular weight of the larger molecules in the feedstocks. Molecules having boiling points less than +525°C can either be used directly as components in hydrocarbon fuel products (gasoline, jet fuel) or as feedstocks for other processes (catalytic cracking, catalytic reforming). Therefore an important analysis is the characterization of reaction products by distillation to determine the mass fraction boiling above 525°C, which still remains to be converted.

Upgrading studies in our laboratory have focussed on hydroprocessing. The +525°C pitch content of liquid products from these studies is frequently determined by the time consuming ASTM D-1160 vacuum distillation method (1). Even with automated equipment, it often takes the major part of a day to perform one analysis. As a result there is considerable interest in a more rapid method which would provide similar information, thereby making the analysis of a greater number of samples feasible. The purpose of this communication is to describe a correlation between the +525°C pitch content of the hydrocracker reaction products and the microcarbon residue (MCR).

EXPERIMENTAL METHODS

The +525°C pitch content was determined by D-1160, using a Herzog model MC 630 automated vacuum distillation apparatus. Automated equipment, Alcor model MCRT, was also used for the microcarbon residue determinations.

Microcarbon residue, ASTM method D-4530 is a measure of the coke forming tendency (during pyrolysis in nitrogen) of a material (2). During analysis, the sample (a hydrocracked reaction product) is heated to 500 °C in a glass vial. The volatile portion is driven off and the remaining residue is weighed. The MCR technique has two advantages over vacuum distillation. First, it is comparatively rapid. Several determinations can be made in one day. Second, the capital cost for automated MCR equipment is only a fraction of that for automated vacuum distillation equipment. MCR values are identical in magnitude (2) to Conradson Carbon Residue (CCR) values (3), but different from Ramsbottom Carbon Residue (RCR) values (4), which have recently been correlated with conversion (5).

RESULTS AND DISCUSSION

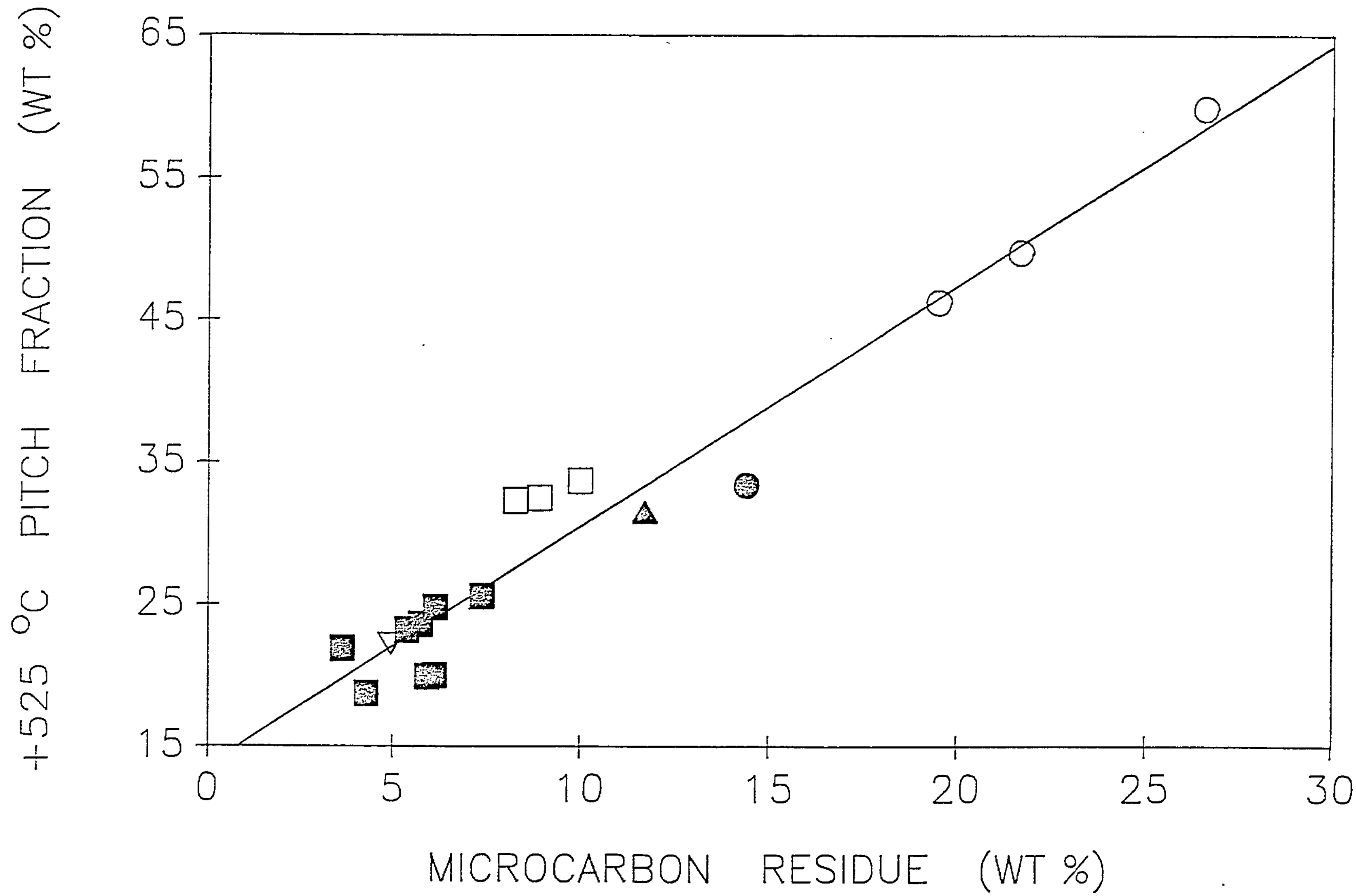
The line through the data points in Figure 1 has a 0.97 correlation coefficient. The equation of the line is

(1) $\text{wt \% } +525^{\circ}\text{C Pitch} = 1.69\ (\text{wt \% MCR}) + 13.5$

It is apparent that a resonably good estimate of the +525°C pitch content can be obtained by substituting the measured MCR value into the correlation given by Equation 1.

The primary phenomenon influencing the relationship between the +525°C pitch content and the tendency to form coke (MCR value) can be seen by examining an example. The data in Table 1 provide a list of the MCR values of several +525°C pitch fractions which were distilled from hydrocarbon reaction products, that had been produced at different catalytic hydrocracking processing conditions. It is apparent that the MCR values for all the hydrocracked +525°C pitch fractions are generally in the neighborhood of 30 wt %. If one assumes that the MCR value for the -525°C distillate portion of the hydrocracker reaction product is negligible compared with the values listed in Table 1, then a correlation between the +525°C pitch and the MCR values of the total hydrocracker reaction product would be expected.

Table 2 gives the +525°C pitch and MCR values for two different feedstocks. These data points do not fit the correlation given in Figure 1. This can be explained in terms of current ideas about the molecular structure of bitumen and heavy oils. These molecules are considered to be composed of a nucleus of condensed rings to which are attached a number of aliphatic side chains. Distillation residue from feedstocks will be composed of molecules that have both


+525 °C PITCH FRACTION (WT %)
65
55
45
35
25
15
0
5
10
15
20
25
30
MICROCARBON RESIDUE (WT %)

condensed ring nuclei and side chains. However, distillation residue from hydrocracked reaction products, will consist primarily of condensed rings. Presumably, the side chains will have been removed during the hydrocracking reaction.

In contrast when the volatile matter is removed during the MCR determinations, the side chains will be volatilized from feedstocks. However, no side chains will be present to be volatilized from products. Therefore, the MCR residues from both feedstocks and hydrocracked reaction products will be without side chains.

Since the mass fraction of vacuum distillation +525^{O}C pitch is proportional to both condensed rings plus side chains while MCR is only proportional to condensed rings, feedstocks would not be expected to follow the same correlation as the correlation for hydrocracked reaction products. The above reasoning suggests that the success of the correlation shown in Figure 1 depends upon the hydrocracking reaction conditions being sufficiently severe to remove the majority of the side chains during the hydrocracking process.

The linear correlation in Figure 1, based on MCR is also consistent with that of McDaniel, Lerman, and Peck(5) which is based on RCR. For a given sample, magnitudes of RCR and MCR will be considerably different if the residue is small (0.01 - 0.1 wt %). However, for the range of values encountered in these studies (1 - 20 wt %) RCR and MCR have similar magnitudes (2,4).

The MCR value of the pitch depends on the processing environment. Table 3 shows the MCR values of +525^{O}C pitch fractions from reaction products that were processed at different thermal (non-catalytic) hydrocracking conditions. The MCR values are generally in the neighborhood of 45. Table 4 gives the MCR value of a pitch from a coprocessed reaction product. Coprocessing is simultaneous coal hydrogenation and vacuum residuum hydrocracking. The MCR value of this pitch is greater than 80 wt %. Clearly the pitches described in Tables 3 and 4 are different than the catalytic hydrocracked pitches described in Table 1.

Differences in the product quality that could influence MCR values are readily identifiable. For example the atomic hydrogen to carbon (H/C) ratios in the total catalytic hydrocracked reaction products (not H/C ratios of the pitch) have an average of 1.63, whereas those for the thermally hydrocracked reaction products have an average of 1.43. It is possible that hydrogen transfer reactions may decrease the amount of residue formed during MCR determinations. If two samples had the same +525°C pitch content, the one with the greater H/C ratio would be expected to form the least amount of residue. The coprocessed pitch sample is different in that it will contain unconverted coal solids. The MCR value of these solids is expected to be very large (perhaps approaching 100 wt %). Therefore it is expected that these unconverted coal solids would cause MCR values to be substantially greater for the coprocessed pitch than for pitches from hydrocracked bitumen or heavy oil. In coprocessing one of the factors affecting the MCR value of the pitch would be the feedstock ratio of coal to vacuum resid.

Some consideration was given to improving the correlation in Figure 1 by accounting for the product quality (specifically the H/C ratio of the product). For example, Equation 2 was found to correlate the + 525°C pitch content in the product.

$$\text{(2)} \qquad \text{wt \% +525}^{\circ}\text{C Pitch} = 1.93\ (\text{wt \% MCR}) - 9.45\ (\text{H/C}) + 29.6$$

When the predicted values from Equation 2 were compared with the corresponding measured values, the resulting correlation coefficient was essentially the same as the correlation coefficient for Figure 1. Since both equations predict similar results, and since additional analyses (H and C) are required to use Equation 2, Equation 1 is recommended.

CONCLUSIONS

In summary, the correlation in Figure 1 has been attributed to two factors. First, it has been assumed that only the pitch contributes to the formation of residue (MCR). Second, hydrogen transfer from the distillate to the pitch may become increasingly important as the pitch content of the sample diminishes, if hydrogen transfer decreases the amount of residue formed.

Although the correlation in Figure 1 may not be universal for all substances (eg. feedstocks), it does appear to be valid for hydrocracked reaction products from bitumen and heavy oils. Since these form an important class of materials, Figure 1 should find considerable use as a relatively rapid and inexpensive characterization method.

ACKNOWLEDGEMENT

The authors would like to acknowledge the contribution of Dr. James F. Kelly, who provided the co-processing data.

REFERENCES

1. ASTM Method D-1160, "Distillation of Petroleum Products at Reduced Pressures", Annual Book of ASTM Standards - Petroleum Products, Lubricants, and Fossil Fuels, 5.01 578-590 (1987).

2. ASTM Method D-4530, "Micro Carbon Residue of Petroleum Products", Annual Book of ASTM Standards - Petroleum Products, Lubricants, and Fossil Fuels, 5.02 585-590 (1987).

3. ASTM Method D-189, "Conradson Carbon Residue of Petroleum Products", Annual Book of ASTM Standards - Petroleum Products, Lubricants, and Fossil Fuels, 5.01 137-143 (1987).

4. ASTM Method D-524, "Ramsbottom Carbon Residue of Petroleum Products", Annual Book of ASTM Standards -Petroleum Products, Lubricants, and Fossil Fuels, 5.01 279-289 (1987).

5. N.K. McDaniel, D.B. Lerman, and L.B. Peck, "Hydrocracker Performance Correlated from Actual Runs", Oil and Gas J. 86 (22) 61-66 (1988).

CAPTION

Figure 1: Weight percent of +525^{O}C pitch in a sample versus weight percent of microcarbon residue . Open circles represent data points from thermal hydrocracking with Cold Lake heavy oil. Open and solid squares represent data points from catalytic hydrocracking with Athabasca bitumen and Boscan heavy oil respectively. The solid circle and solid triangle represent thermal cracking with Athabasca bitumen and Boscan heavy oil respectively. The open inverted triangle represents coprocessing.

TABLE 1

MCR OF THE +525^{o}C PITCH FRACTION
IN CATALYTIC HYDROCRACKING REACTION PRODUCTS

FEEDSTOCK	MCR (wt %)
Athabasca	29.3
Athabasca	25.5
Athabasca	27.3
Boscan	31.8
Boscan	31.6
Boscan	31.2
Boscan	29.0
Boscan	29.4
Boscan	32.3
Boscan	30.1
Boscan	36.8

TABLE 2

FEEDSTOCK CHARACTERISTICS

	Feedstock	
	Athabasca	Boscan
MCR of feedstock (wt %)	16.2	15.5
+525°C pitch in feedstock (wt %)	52.0	54.6
MCR of pitch (wt %)	32.2	29.2

TABLE 3

MCR OF THE +525°C PITCH FRACTION
IN THERMALLY HYDROCRACKED REACTION PRODUCTS

FEEDSTOCK	MCR (wt %)
Athabasca	41.4
Boscan	50.9
Cold Lake	42.9
Cold Lake	44.7
Cold Lake	44.1

TABLE 4

MCR OF THE +525^{o}C PITCH FRACTION IN COPROCESSING REACTION PRODUCTS

Feedstock Mixture	70 % Cold Lake Vacuum Resid 30 % Forestburg Coal
MCR of pitch (wt %)	86.7